MOCVD GAS-PHASE DEPOSITION APPARATUS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is the US national phase of PCT
application PCT/DE2004/000315, filed 20 February 2004, published 07
October 2004 as WO 2004/085702, and claiming the priority of German
patent application 10312768.2 itself filed 21 March 2003 and German
patent application 10325629.6 itself filed 6 June 2003, whose
entire disclosures are herewith incorporated by reference.

FIELD OF THE INVENTION

The invention relates to an apparatus for depositing
compounds on a substrate by means of metal organic gas-phase
deposition.

BACKGROUND OF THE INVENTION

Metal-organic gas-phase deposition (metal-organic
chemical vapor deposition: MOCVD) is a method of making layer
structures of a complex configuration as can be used in electronic
components, for example, high-speed transistors for cell phones or
light-emitting diodes. By contrast to known silicon structures,
these structures are composed not of one element but from two or
even more elements. They can be referred to therefore also as
compound semiconductors. The metal organic gas-phase deposition is
carried out in a so-called MOCVD apparatus.

With the MOCVD apparatus, nitride layers among others can
be deposited and can be comprised of two elements, like for
example, GaN, InN or AlN or from more elements like for example

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GaInN or AlGaN. These compounds are referred to as binary or
terniary systems for the monocrystalline deposition of nitride
compounds, sapphire (Al_2O_3) or silicon carbide (SiC) or silicon,
which have similar crystal characterstics to the nitrides are used
as substrates.

The group III nitrides include through their
representatives a semiconductor system with direct band gaps of 1.9
eV for InN to 6.2 eV for the aluminum nitride AlN.

These nitride layers are economically very significant
since they can emit light in the blue part of the visible spectrum
upon electrical excitation and thus can be used to make
optoelectronic components which are useful in the corresponding
energy range. As an example of this are pn light-emitting diodes
on the basis of GaN.

For metal organic gas-phase deposition of nitride layers
one requires gas-phase compounds of gallium, indium or aluminum as
well as NH_3 as so-called precursors. In the case of gallium, a
metal organic compound, for example trimethylgallium (TMG) is used.
By means of a carrier gas, for example hydrogen, the precursor is
carried into a reaction compartment of the apparatus. There is
found the substrate, a monocrystalline very thin disk (wafer) which
can be heated. The wafer is mounted so as to rotate on a so-called
susceptor to produce a uniform distribution of temperature and
precursor in the gas phase over the substrate. With an infrared
radiator or high-frequency heating the susceptor and the substrate
are heated. The temperature of the substrate reaches about 1500°C

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depending upon which material systems is deposited. This region is also designated as the hot zone.

For the deposition upon the substrate, the precursor is transformed. This occurs in part already in the gas phase as a result of the heat which is emitted by the substrate or by impingement of molecules of the carrier gas thereon. The molecular fragments deposit upon the substrate surface. As a result of the high temperature the original precursor compounds decompose and react to form new compounds, for example, GaN, InN or AlN. In this manner a new layer grows upon the wafer in atomic layer after atomic layer as GaN, InN or AlN. The residues of the starting molecules, for example methyl groups from TMG and hydrogen combine partly with one another to form methane. Molecules which do not deposit or adhere and molecular fragments are released from the surface and like the methane are carried off with the carrier gas stream and are discharged from the MOCVD apparatus to a gas cleaning system, a so-called scrubber, for removal.

An MOCVD apparatus usually has two gas inlets and provisions for dividing the gas streams which are to be introduced into the apparatus so that an instantaneous mixing within the apparatus, which could lead to the formation of acid-based adducts prematurely, can be avoided. For this purpose a partition or separator plate can be so arranged downstream of the gas inlets of the apparatus that the MOCVD apparatus is compartmented into an upper and a lower space. Outside the apparatus, gas supply lines or manifolds are provided which can be connected to supply vessels.

In these supply vessels the starting materials are held in readiness, for example on the one hand the metal organics and on the other hand group V or group VI compounds.

A drawback is that up to now it has not been possible to flexibly distribute the gases within the compartments of the apparatus.

In the formation by the aforedescribed technology of, for example, group III nitride layers by means of gas phase deposition in an MOCVD apparatus, precursors together with their carrier gases (H_2, N_2, argon) are each separately fed into the apparatus. The gas streams are first mixed in the hot zone of the apparatus in order to ensure a stable nitride surface at which at the growth temperature nitrogen may be volatile, the carrier gas/NH_3 mixture (Group V compounds) according to the state of the art is locally introduced more closely to the growth surface at the substrate than the carrier gas/metal-organic mixture. As a consequence the hot surface of the substrate will cause nitrogen to be liberated from the ammonia and to be available for reaction upon the substrate. This approach has also been used for the deposition of other compounds as well.

A drawback of this system is that the nitrides formed also tend to deposit rapidly parasitically on the hot walls of the apparatus. The nature and thicknesses of these deposits vary in the course of the method. The parasitic deposits cause variations in the growth on the substrate by catalytic decomposition of the starting compound and the reduction in concentration in the gas

phase as a result. Since the deposited compounds are of a dark
coloration, they influence the gas phase temperature and the
surface temperature of the substrate. The nitride layers can thus
not be reproducibly formed on the substrate.

5   The parasitic deposits flake off from the walls after a
short time and the particles can then fall from the parasitic-
deposit-coated parts of the apparatus upon the substrate or the
sample and can have a detrimental effect on the characteristics of
the layer or layers to be applied there.

10   As a solution to this problem, the parts of the
apparatus, which have been coated by the parasitic deposition and
which may come into contact with the substrate, are replaced or
cleaned as soon as the parasitic deposit has accumulated to a
critical level.

15   This however is detrimentally expensive since in the
interim the apparatus cannot be used.

                      OBJECT OF THE INVENTION
          The object of the invention is to provide an apparatus
for depositing a compound on a substrate by means of metal organic
20 gas-phase deposition without such parasitic deposits occurring.

                    SUMMARY OF THE INVENTION
          According to the invention, in the method a first mixture
of at least carrier gas and at least one metal organic compound and
a second mixture of at least one carrier gas and at least one Group
25 V compound or Group VI compound are used, whereby both mixtures are
separately admitted into an apparatus for depositing the compound

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upon the substrate. The method is characterized in that at least
one metal organic compound is introduced between the substrate and
the Group V or Group VI compound. The at least one metal organic
compound is thus fed into the apparatus at a location which is
closer to the substrate than the Group V or Group VI compound.

       Advantageously this has the effect that the thickness of
the parasitic deposition is significantly reduced since the deposit
is formed practically exclusively where it is desired, namely upon
the substrate. The deposition rate as a rule is increased and the
coatings or layers are of higher purity by comparison with layers
of coating which are deposited by state of art techniques.

       The particle formations on the wall and the ceiling of
the apparatus are reduced to a minimum. Many layers can be
deposited reproducibly before parts coated by parasitic deposition
of the apparatus must be replaced in an expensive operation and
without the danger that materials separating from parasitic
deposits will flake off and contaminate the deposited layer.

       The metal organic compound can be selected from a Group
II compound or a Group III compound or a Group IV compound. Only
examples, barium/strontium compounds (Group II) or
trimethylgallium, trimethylaluminum and trimethylindium (Group III)
or titanium isopropoxide (Group IV) are specifically mentioned only
by way of example. As Group V compounds NH_3 and/or AsH_3 and/or PH_3
can be used and as Group VI compounds, oxygen or diethyltelluride
can be used.

It will be self-understood that the method is not limited to a selection from such compounds. Rather the method can basically be used for the deposition of compounds on a substrate by means of metal organic gas-phase deposition generally. As a carrier gas for the compounds, hydrogen and/or nitrogen and/or argon are to be considered.

For the deposition of for example GaN, trimethylgallium is selected as a Group III compound and NH_3 as the Group V compound with hydrogen as the respective carrier gas in each case.

In this case, the metal organic/carrier gas mixture is introduced between the substrate and the point at which the NH_3/carrier gas mixture is introduced. It is however possible without limiting the invention to carry out the process according to the invention with other compounds to avoid parasitic deposition.

An MOCVD apparatus has at least two gas inlets, a first for a first mixture and at least one second for a further mixture. The gases themselves derive from the supply vessels. Between the gas inlets of the apparatus and the supply vessels for the gases there are, according to the invention, means, especially at least two three-way valves, arranged in so-called gas-collecting lines. There can however also be suitable quick-connect couplings in these lines.

This enables advantageously the apparatus to be connected to the supply vessels and the gases to be flexibly introduced into the various compartments of the MOCVD apparatus in a flexible

manner without each time requiring the apparatus to be separated
from the supply vessels to be newly connected thereto.

In other words the operator of such an apparatus is able
to supply gases based upon his requirements conveniently and
flexibly into the parts of the apparatus at which they are
required. For this purpose inlets for the gas mixtures can rapidly
be exchanged for one another.

It is also conceivable for this purpose to provide other
structural modifications to the apparatus.

BRIEF DESCRIPTION OF THE DRAWING

Below the invention will be described in greater detail
based upon several embodiments or examples and the accompanying
five Figures in which:

FIG. 1 is a schematic perspective view of an MOCVD
apparatus according to the invention;

FIG. 2 is a section through the apparatus of FIG. 1;

FIG. 3 illustrates mixing of gases in the apparatus;
http://www.allsitesaccess.com/more_cumfiesta.htm?id=ndmariod

FIGS. 4a and 4b are graphs illustrating the prior art and
the present invention, respectively; and

FIG. 5 is a schematic illustration of the invention.

SPECIFIC DESCRIPTION

FIG. 1 shows schematically an MOCVD apparatus according
to the state of the art with two gas inlets 4, 5 for an upper
compartment and a lower compartment. Precursors are separated from
one another by a partition plate 1 and are supplied to a substrate

2 to be coated. The MOCVD apparatus is compartmented by the
partition 1 into an upper chamber and a lower chamber downstream of
the gas inlets 4, 5. The substrate 2 can for example be a two unit
wafer. Self-understood, moreover, is that the method is not
limited to particular sizes or shapes of the substrate. The
substrate 2 is mounted in a susceptor 6 here formed as a rotatable
plate. The walls of the apparatus have only been indicated in the
drawing. That is, only one wall has been illustrated
substantively, namely the wall 3 in the present case. The front
walls in the direction of view of the roof have not been
illustrated to allow a look into the interior of the apparatus.

FIG. 2 is a cross section through the apparatus along an
imaginary line between the inlets and a cooling unit 7 located
upstream of the susceptor (not shown). The cooling unit 7 has been
shown only schematically in FIG. 2. In the present case, the gas
inlet 5 is provided to introduce the metal organic/carrier gas
mixture (TMG/H_2) and the gas inlet 4 for the NH_3/carrier gas mixture
(NH_3/H_2). After the gases are admitted into the apparatus the two
gas streams remain separated from one another initially by the
partition 1 until they mix downstream of the partition plate 1 and
contact the substrate on the susceptor. The metal organic/carrier
gas mixture is introduced between the substrate and the NH_3/carrier
gas mixture.

FIG. 3 shows the mixing of the reactants above the
cooling unit 7 shown only schematically and closely upstream of the
susceptor 6. The more dense ammonia/carrier gas mixture diffuses

in the direction of the substrate on the susceptor 6 where it mixes with the metal organic/carrier gas mixture. On and upstream of the substrate such that the decomposition of the precursor is catalytically accelerated, there is a precipitation of GaN. The total gas mixture does not reach the roof of the apparatus so that there too a parasitic deposition of GaN is avoided.

FIG. 4a shows the course of the deposition of GaN as will arise in the state of the art. The X axis shows the local coordinate along a substrate or a wafer. The wafer is represented by the bar. The deposition rate after an hour amounts to only about 1.3 micrometer GaN.

The process according to the invention, in which the TMG/H_2 mixture is introduced according to the invention between the substrate and the NH_3 carrier gas mixture and thus locally more proximal to the substrate, enables on average a much higher deposition rate of about 4 to 5 micrometers GaN. Because of the rotatable susceptor 6, the deposit can be uniformly distributed across the wafer (FIG 4b). The higher deposition rate ahead of the wafer enables the deposition of GaN with much higher purity on this wafer.

The higher deposition rate in this latter case is a result of the fact that the gas phase is not diminished as a result of parasitic deposition on the apparatus walls. The gases therefore remain available for deposition on the substrate.

The deposition illustrated in FIGS. 2-4 of GaN is only given by way of example. As another example of the present invention is the deposition of zinc telluride.

In this case, between the substrate and the Group VI compound diethyltelluride, the Group II compound dimethylzinc is fed into the apparatus.

It is also possible in the deposition of the dielectric (Ba, Sr) titanate, for a mixture of two or three metal organics to be fed between oxygen and the substrate into the apparatus. The metal organics comprise for example a mixture of diketonate of barium and strontium and aloxides of titanium, for example, titanium isopropoxide. Thus between the substrate and the oxygen, of the Group VI compounds, the mixture of these metalorganics is fed into the apparatus.

Furthermore, it is possible to produce respective compounds in layer form each from a suitable combination of metal organics and Group V or Group VI compounds as has been given in Table 1.

FIG. 5 shows a switching device for the gas inlets of an MOCVD apparatus. The collecting line 52 is connected with a supply vessel (not shown) for a carrier gas/metal organics gas mixture and contains the pneumatic 3/2-way valve V2. The collect line 51 is connected with a supply vessel or carrier gas/Group V or Group VI gas mixture and extends through the pneumatic 3/2-way valves [3 port/2 position valve] V1. The valves V1 and V2 are connected via the respective lines with the upper compartment 4' and the lower

compartment 5' via the respective gas inlets. In the pressureless state of valve V2 the valve opens into the upper compartment and in the depressurized state of valve V1, it opens into the lower compartment 5' (see FIG. 5). The gases are introduced in the state of the art technique into the apparatus.

Both valves V1 and V2 are connected to a N_2 pressure line 53 over a manually operated valve V3 and can be switched over thereby. In that case, the mixture of the carrier gas or carrier gases and at least one metal organic is then fed under pressure into the compartment 5' and thus between a substrate on the susceptor 6 and a mixture of carrier gas or gases and at least one Group V or Group VI compound. The last-mentioned gas mixture is then fed into the compartment 4'. The partition plate 1 in FIG. 1 has only been shown representationally and extends as shown in FIGS. 1 and 3 up to the susceptor 6. Thus it is ensured that the different gas mixtures will never be present simultaneously in one and the same compartment 4' and 5'. This kind of improvement enables as reliable and at the same time flexible feed of the gas mixture into the upper and lower compartment 4', 5' of the apparatus.

Parts list:

3/2-way valves (V1, V2): 1/4 inch VCR-FFF

3/2-way valve (V3) hand-operated, built-in panel valves (Bosch) 0820 402 024 3/2 WV NG4 (1/8 inch)

Stainless steel pipe 8/8 inch electropolished

Pneumatic tubing 1/8 inch

Table 1

Layer Compound	Metal Organic	Group V/Group VI Compound	Carrier Gas
Aluminumgallium arsinide ((AlGa)As)	TMAl(Trimethylaluminum), TEAl(Triethylaluminum), TMGa(Trimethylgallium), TEGa(Triethylgallium	AsH$_3$(Arsine) TBAs (Tert-butylarsine)	H$_2$, N$_2$, Ar
Galliumarsenide (GaAs)	TMGa, TEGa	AsH$_3$, TBAs	H$_2$, N$_2$, Ar
Aluminumarsenide (AlAs)	TMAl, TEAl	AsH$_3$, TBAs	H$_2$, N$_2$, Ar
Galliumindiumarsenide (AlIn)As)	TMGa, TEGa, TMin	AsH$_3$, TBAs	H$_2$, N$_2$, Ar
Aluminumindiumarsenide ((GaIn)As)	TMAl, TEAl, TMln	AsH$_3$, TBAs	H$_2$, N$_2$, Ar
Indiumphosphide (InP)	TMln	PH$_3$, TBP	H$_2$, N$_2$, Ar
Aluminumgalliumindium-phosphide(AlGa lnP)	TMAl, TEAl, TMGa, TEGa, Tmln (Trimethylindium dium)	PH$_3$(Phosphino), TBP (Tertiarbutyl phoshine)	H$_2$, N$_2$, Ar
Galliumindium phosphide ((GaLn)(P)	TMGa, EGa,TMln	Ph$_3$, TBP	H$_2$, N$_2$, Ar
Aluminumindium phosphide((Alln)(P)	TMAl,EAl, TMln	PH$_3$, TBP	H$_2$, N$_2$, Ar
Galliumindiumarsenidephosphide (((Galn)(AsP))	TMGDa, TEGa, TMln	AsH$_3$, TBAs, PH$_3$, TBP	H$_2$, N$_2$, Ar
Aluminumgalliumindiumarsenide phosphide(Al Galn)(AsP))	TMAl, TEAl, TMGa, TEGa, TMln	AsH$_3$, TBAs, PH$_3$, TBP	H$_2$, N$_2$, Ar
Aluminumnitride (Aln)	TMAl, TEAl	NH$_3$ (Ammonia)	H$_2$, N$_2$, Ar
Galliumnitride (GaN)	TMGa, TEGa	NH$_3$	H$_2$, N$_2$, Ar

Indiumnitride (InN)	TMIn	NH$_3$	H2, N$_2$,, Ar
Aluminumgalliumindiumnitride ((AlGaIn)(N)	TMAl, TEAl,TMGa,TEGa, TMIn	NH$_3$	H$_2$, N$_2$, Ar
Galliumindiumnitride((GaIn)(N)	TMGa,TEGa,TMIn	NH$_3$	H$_2$, N$_2$, Ar
Galliumantimonide (GaSb)	TMGa,TEGa	TMSb (Trimethyl antimony) TESb (Triethyl-antimony)	H$_2$, N$_2$, Ar
Aluminumantimonide (AlSb)	TMAl, TEAl	TMSb, TESb	H$_2$, N$_2$, Ar
Indiumantimonide (InSb)	TMIn	TMSb, TESb	H$_2$, N$_2$, Ar
Aluminumindiumantimonide (AlIn)Sb))	TMAl, EAl, TMIn	TMSb, TESb	H$_2$, N$_2$, Ar
Galliumindiumantimonide ((GaIn)Sb))	TMGa, TEGa, TMIn	TMSb, TESb	H$_2$, N$_2$, Ar
Galliumarsenideantimonide (Ga(AsSb))	TMGa,TEGa	PH$_3$ TBP, TMSb, TESb	H$_2$, N$_2$, Ar
Aluminumarsenideantimonide (Al(AsSb))	TMAl, TEAl	AsH$_3$, TBAs,TMSb, TESb	H$_2$, N$_2$, Ar
Indiumarsenideantimonide (In(AsSb))	TMIn	AsH$_3$, TBAs, TMSb, TESb	H$_2$, N$_2$, Ar
Galliumindiumarsenide-antimonide(GaIn)(AsSb))	TMGa,EGa, TMIn	AsH$_3$, TBAs, TMSb, TESb	H$_2$, N$_2$, Ar
Galliumphosphideantimonide (GaPSb))	TMGa, TEGa	PH$_3$ TBP, TMSb, TESb	H$_2$, N$_2$, Ar
Indiumphosphideantimonide (In(PSb))	TMIn	PH$_3$ TBJP, TMSb, TESb	H$_2$, N$_2$, Ar
Indiumphosphidearsenide-antimonide (In(PAsSb))	TMIn	PH$_3$ TBP, AsH$_3$ TBAs, TMSb, TESb	H$_2$, N$_2$, Ar
Cadmiumtelluride (CdTe)	DMCd (Dimethyl-cadmium)	DETe Diethyltellurium) DMTe Dimethyl-tellurium, DIPe (Diisopropyl-tellurium)	H$_2$, N$_2$, Ar
Mercurytelluride (Hg/Te)	Hg (Mercury)	DETe	H$_2$, N$_2$, Ar
Cadmiummercury telludride((CdHg)Te)	DMCd,HGD	DETe	H$_2$, N$_2$, Ar

Zincsulfide (ZnS)	DMZn (Dimethyl-zinc), DEZn (Diethylzinc)	H_2S Hydrogen-sulfide,DES (Diethylsulfide), DTBS (Ditert-butylsulfide)	H_2, N_2, Ar
Zincselenide(ZnSe)	DMZn (Dimethylzinc), DEZn (Diethylzinc)	DMSe (Dimethyl-selenide), DESe Diethylsselenium, DIPSe(Diisopropyl selenium), DTBSe (Ditert-butylsselenium)	H_2, N_2, Ar
Bariumstrontiumtitanate ((BaSr)TlO$_3$)	Ba(thd)$_2$, (Barium/Strontium tetramethylheptanedionat), Ba(hfa)$_2$ (Barium//Strontiumhexafluoroaetylacetone), TIP (Titaniumtetrakisisopropoxide), TTB (Titaniumetrakisterbutoxide),	O_2 (Oxygen),O_3 (Ozone), N_2O (laughing gas)	N_2, Ar
leadzirconatetitanate (Pb(ZrTi)O$_3$)	TEL (Tetraethyl lead), TEL (Tetraphenyllead Pb(thd)$_2$ (Leadtetramethylheptanedionate), ZIP (Zirconiumtetrakisiso-propoxide) TIP, TTB	O_2	